UNCLASSIFIED

AD 262 330

Reproduced by the

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA

DEPARTMENT OF DEFENSE
UNITED STATES OF AMERICA

UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

AD No. 262330
ASTIA FILE COPY

①

NATIONAL BUREAU OF STANDARDS REPORT

7303

HEATS OF FORMATION OF TWO ISOMERS OF DIFLUORODIAZINE

by

George T. Armstrong and Sidney Marantz

Heat Measurements Section
Heat Division
National Bureau of Standards
Washington 25, D. C.

61-4-4

XEROX

203 400

FILE COPY
Return to
ASTIA
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA
Attn: TISSS

ASTIA
RECEIVED
AUG 31 1961
TIPDR
A

NBS

S. DEPARTMENT OF COMMERCE
ATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

Functions and Activities

The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to government agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. Research projects are also performed for other government agencies when the work relates to and supplements the basic program of the Bureau or when the Bureau's unique competence is required. The scope of activities is suggested by the listing of divisions and sections on the inside of the back cover.

Publications

The results of the Bureau's research are published either in the Bureau's own series of publications or in the journals of professional and scientific societies. The Bureau itself publishes three periodicals available from the Government Printing Office: The Journal of Research, published in four separate sections, presents complete scientific and technical papers; the Technical News Bulletin presents summary and preliminary reports on work in progress; and Basic Radio Propagation Predictions provides data for determining the best frequencies to use for radio communications throughout the world. There are also five series of nonperiodical publications: Monographs, Applied Mathematics Series, Handbooks, Miscellaneous Publications, and Technical Notes.

A complete listing of the Bureau's publications can be found in National Bureau of Standards Circular 460, Publications of the National Bureau of Standards, 1901 to June 1947 ($1.25), and the Supplement to National Bureau of Standards Circular 460, July 1947 to June 1957 ($1.50), and Miscellaneous Publication 240, July 1957 to June 1960 (Includes Titles of Papers Published in Outside Journals 1950 to 1959) ($2.25); available from the Superintendent of Documents, Government Printing Office, Washington 25, D. C.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT **NBS REPORT**

0302-11-03405 June 1961 7303

HEATS OF FORMATION OF TWO ISOMERS OF DIFLUORODIAZINE

by

George T. Armstrong and Sidney Marantz

Heat Measurements Section
Heat Division

Technical Report
to
Bureau of Naval Weapons
Department of Defense

Order Number 19-61-8007 Weps

IMPORTANT NOTICE

NATIONAL BUREAU OF STANDARDS REPORTS are usually preliminary or progress accounting documents intended for use within the Government. Before material in the reports is formally published it is subjected to additional evaluation and review. For this reason, the publication, reprinting, reproduction, or open-literature listing of this Report, either in whole or in part, is not authorized unless permission is obtained in writing from the Office of the Director, National Bureau of Standards, Washington 25, D. C. Such permission is not needed, however, by the Government agency for which the Report has been specifically prepared if that agency wishes to reproduce additional copies for its own use.

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

TABLE OF CONTENTS

Page No.

Abstract i

1.0 Introduction 1

2.0 Experimental Procedures 1

    2.1 Materials 1
    2.2 Calibration 2
    2.3 Experimental Heat Measurements 6

3.0 Calculation of Experimental Results 6

4.0 Heats of Formation of N_2F_2 Isomers 8

5.0 Bond Energies 9

6.0 References 12

Abstract

The heats associated with the reaction of

~~$$N_2F_2(g) + \frac{8}{3}NH_3(g) = 2NH_4F(c) + \frac{4}{3}N_2(g)$$~~ N2F2 with NH3

were observed for two mixtures containing the trans and the "active" isomers difluorodiazine (N_2F_2) in different proportions. From the observed heats of reaction the heats of formation, ΔHf^{o}_{298}, were determined to be * ~~+19.4 ±1.3 and +16.4 ±1.2 kcal mole^{-1}~~ for the trans and the "active" isomers, respectively. The bond energies in the two substances are discussed in terms of the possible molecular configurations.

* + / 19.4 + or − 1.3 and + / 16.4 + or − 1.2 kcal mol

LIST OF TABLES

Page No.

1. Calibration of Calorimeter 3

2. Experimental Results of Combustion Experiments . . 5

3. Calculations of Combustion Experiments 7

1.0 Introduction

The continuing interest in the thermochemistry of N-F compounds has led us to make a determination of the heats of formation of two isomers of N_2F_2. The techniques applied had been previously worked out for NF_3 [1,2][1] and N_2F_4 [3], and in their application the N_2F_2 compounds presented no unusual experimental problems. The isomers studied were trans-1,2-difluorodiazine and a more reactive isomer. There is some uncertainty as to whether the latter is cis-1,2-difluorodiazine or 1,1 difluorodiazine [4]. Because of the uncertainty concerning structure still associated with this isomer it is referred to in this report as the "active" isomer of N_2F_2. This designation was selected because it emphasizes the greater chemical reactivity of the isomer in comparison with the trans species.

The heats of formation of these two compounds (and the third possible one as well) are of interest intrinsically because of the information they may yield about the variation in the N-F bond strength in varying molecular environments.

The heat of isomerization, 3.0 kcal $mole^{-1}$, of the isomers, which we find for the difference in the heats of formation, is in agreement with our calculation of the results of equilibrium measurements made by Colburn, et al [5].

Although it would have been desirable to have larger quantities and more nearly pure starting materials, it is felt that the results obtained are unambiguous, and sufficiently reliable to be useful in synthetic applications. Moreover, this work marks the first experimental measurement of the heats of formation of the N_2F_2 isomers.

2.0 Experimental Procedures

2.1 Materials

Two samples of N_2F_2, one (Sample I) consisting principally of the trans, and the other (Sample II) consisting principally of the "active" isomer were presented to us by Dr. Vernon H. Dibeler of the Mass Spectrometry Section of the National Bureau of Standards, who had received them through the courtesy of Dr. Charles S. Cleaver of the E. I. du Pont de Nemours Company.

---

[1] Numbers in brackets refer to references at the end of this report.

Analyses of the materials were made after completion of the experiments. Dr. John T. Herron and Mrs. Sharon Lias made mass analyses independently using different mass spectrometers, and Dr. S. C. Wait, Jr. examined the materials with an IR Spectrophotometer. There were some discrepancies in the different analyses, and judgments were made concerning final specifications of impurities. These judgments were based mainly on the type of instrument used and on the experience of the analyst with these particular compounds.

The following analyses were assigned to the samples: I, 0.1% N_2O, 10.0% "active"-N_2F_2, 89.9% trans- N_2F_2; II, 0.4% N_2O, 0.1% SiF_4, 0.1% CO_2, 91.6% "active"-N_2F_2, 7.8% trans-N_2F_2.

It is not possible to state accurately what changes in the samples may have occurred during the course of the experiments. A slow conversion of the samples to the equilibrium mixture would be expected [5]. However, there was no chronological trend in the values measured for sample I. The samples were stored at -100°C when not being used. Because the heats of formation of the two isomers do not differ very much, the calculations are not strongly dependent upon the isomeric ratios in the samples.

Only 4.2 grams of sample I and 2.2 grams of sample II were available. The small size of the samples precluded any attempt at further purification.

The ammonia was a commercial high purity grade stated to be 99.9 percent pure. A rough chromatographic analysis indicated impurities in the NH_3 amounting to probably less than 0.1 percent.

2.2 Calibration

The calorimeter was calibrated with benzoic acid (NBS Standard Sample 39h) in five experiments summarized in Table 1. The heating value used for the standardizing material was 26.4338 kj/gram mass (weight in vacuum). The final temperature to which the calibration is referred is 28 °C. In Table 1, m_s is the mass of benzoic acid; ΔR_c is the corrected thermometer resistance change; and E_s is the energy equivalent of the standard calorimeter. The correction term, e, is the difference between the energy equivalent of the calorimeter as used in the calibration experiments and the standard calorimeter used for the combustion experiments. It includes heat capacity terms for 1 ml of water, for the platinum crucible, for the benzoic acid pellet, and for the 30 atmospheres of oxygen, all present in the calibration experiments, but not in the combustion experiments.

Table 1

Run No.	m_s g	ΔRc ohms	$-e$ j ohm^{-1}	E_s j ohm^{-1}
1	1.49810	0.289963	173.7	136503.4
2	1.50110	.290453	173.2	136538.8
3	1.49886	.290042	172.8	136462.2
4	1.49826	.289862	176.1	136548.2
5	1.50942	.291988	175.8	136565.4
Mean				136524. ±18[a]

---

[a] Standard deviation of the mean.

For each combustion experiment the energy equivalent of the actual calorimeter, E, shown in Column 3, Table 2, was obtained from the mean energy equivalent of the standard calorimeter, 136524 j/ohm, by adding a term e', to adjust for the heat capacities of the gases introduced into the bomb for the experiment. For this purpose the specific heat, C_v, of NH_3 was taken to be 28.47 j mole^{-1} deg^{-1} [6] and that of N_2F_2 was assumed to be similar to that of N_2F_4 for which a value of 63.5 j mole^{-1} deg^{-1} was estimated previously [3].

Table 2

(1) Run No.	(2) e' j ohm^{-1}	(3) E j ohm^{-1}	(4) mass of sample gm	(5) mass of N_2F_2 moles	(6) NH_3 introduced moles	(7) NH_3 recovered moles	(8) ΔR_c ohm
1	39.2	136563	0.93340	0.01429	0.098165	0.043851	0.085518
2	38.4	136562	.86813	.013141	.097863	.051089	.080815
3	39.3	136563	.93070	.014088	.098315	.046038	.085612
4	38.4	136562	.93636	.014174	.095180	.040470	.085722
5	36.4	136560	0.90786	0.13685	0.089695	0.036356	0.081649
6	36.7	136560	.89670	.013517	.090912	.039992	.081228

2.3 Experimental Heat Measurements

The calorimeter and the procedures used in these experiments were identical to those used for the measurements on N_2F_4 [3]. The observed data are shown in Table 2. Measurements 1,2,3 and 4 were made on sample I; measurements 5 and 6 on sample II.

The amount of reaction was based on the weight of sample dosed into the bomb from a monel weighing bulb. The mass of sample is shown in column 4. The number of moles of N_2F_2 introduced, calculated from the mass of sample and its composition, is shown in column 5.

The crystalline product deposited in one experiment with each isomer was examined with an x-ray spectrograph, and found to be, within the 2 percent sensitivity of the method, exclusively NH_4F. The observed weight of NH_4F agreed to about 1 percent with that calculated theoretically, but was not used in the calculation since it leads to less precise results.

Columns 6 and 7 respectively, give the measured quantities of NH_3 introduced and recovered. The corrected resistance thermometer change, ΔRc, caused by the reaction is shown in column 8.

3.0 Calculation of Experimental Results

The results were calculated on the basis that the reaction of the N_2F_2 was equation (1).

$$N_2F_2(g) + \frac{8}{3}NH_3(g) = 2NH_4F(c) + \frac{4}{3}N_2(g) \qquad (1)$$

and are shown in Table 3. ΔE_b, the observed total energy change caused by the bomb reaction, is obtained as the product of E and ΔR_c (Table 2).

Correction terms applied are: q_1, the difference $\Delta H - \Delta E$ for the reaction; q_2, the enthalpy correction to bring the reactants and products to unit fugacity in the ideal gas state; q_3, a heat capacity correction to convert the reaction heat from 28 °C to 25 °C; q_4, the energy of the reactions due to impurities; and q_5, the energy of decomposition of ammonia. The heats of reaction, (ΔH^o_{25}), in joules per mole of N_2F_2 are shown in column 8.

In the calculation of quantities q_1 to q_5, data for the thermal properties of the several substances involved were selected from the literature as before (1). The enthalpy corrections for N_2 and H_2 were neglected as they were demonstrated to be very small. N_2F_2 was treated as an ideal gas.

Table 3

(1) Run No.	(2) ΔE_b j	(3) q_1 j	(4) q_2 j	(5) q_3 j	(6) q_4 j	(7) q_5 j	(8) $-\Delta H^o_{25}$ kj $mole^{-1}$
1	-11678.6	-29.2	-45.3	-1.7	+5.2	-768.5	885.99
2	-110363.3	-36.6	-39.6	-4.1	+5.2	-541.9	886.79
3	-11691.4	-34.2	-44.2	-4.7	+5.6	-679.4	883.61
4	-11706.4	-29.4	-41.8	-4.2	+5.6	-781.2	885.95
		Mean for N_2F_2 (Sample I)					885.59 or 211.7 kcal $mole^{-1}$
		Standard Deviation of the Mean					±0.69 or ±0.2 kcal $mole^{-1}$
5	-11150.0	-27.9	-37.5	-4.3	+21.2	-778.1	875.17
6	-11093.3	-31.9	-37.4	-4.1	+21.2	-687.1	875.33
		Mean for N_2F_2 (Sample II)					875.25 or 209.2 kcal $mole^{-1}$
		Standard Deviation of the Mean					±0.08 or ±0.02 kcal $mole^{-1}$

The heat correction applied for the partial decomposition of NH_3, q_5, was calculated from equation (2) below.

$$q_5 = -\left[\begin{array}{ccc} NH_3 \text{ introduced} & - \; NH_3 \text{ recovered} & - \; \frac{8}{3} N_2F_2 \\ \text{Table 2} & \text{Table 2} & \text{Table 2} \\ \text{Column 6} & \text{Column 7} & \text{Column 5} \end{array}\right] \begin{array}{l} \times \; 11.04 \text{ kcal mole}^{-1} \\ \times \; 4184 \text{ j/kcal}^{-1} \end{array} \qquad (2)$$

The mean heat of reaction for N_2F_2 in Sample I is 885.59 ±0.69 kj mole^{-1} or 211.7 ±0.2 kcal mole^{-1}, and for N_2F_2 in Sample II is 875.25 ±0.08 kj mole or 209.2 ±0.02 kcal mole^{-1}.

4.0 The Heats of Formation of the N_2F_2 Isomers

From the heats of reaction of N_2F_2 in Sample I and N_2F_2 in Sample II are derived the heats of formation of the N_2F_2 isomers. Using ΔHf^{0}_{298} $[NH_3(g)] = -11.04 \pm 0.07$ kcal mole^{-1} [6], and ΔHf^{0}_{298} $[NH_4F(c)] = -111.0 \pm 0.6$ kcal mole^{-1} [7], we conclude that for the sample mixtures studied (corrected for non-N_2F_2 impurities) ΔHf^{0}_{298} $[N_2F_2$ (sample I)$] = 19.1 \pm 1.3$ kcal mole^{-1}, and ΔHf^{0}_{298} $[N_2F_2$ (sample II)$] = + 16.6 \pm 1.2$ kcal mole^{-1}.

As both samples are mixtures of the two isomers, the heats of formation of the samples can be represented in terms of the heats of formation of the pure isomers by means of simultaneous equations (3) and (4).

$$0.900 \; \Delta Hf^{0}_{298} [\text{trans-}N_2F_2] + 0.100 \; \Delta Hf^{0}_{298} [\text{"active"-}N_2F_2] = 19.1 \text{ kcal mole}^{-1} \qquad (3)$$

$$0.078 \; \Delta Hf^{0}_{298} [\text{trans-}N_2F_2] + 0.922 \; \Delta Hf^{0}_{298} [\text{"active"-}N_2F_2] = 16.6 \text{ kcal mole}^{-1} \qquad (4)$$

Solution of eqs. (2) and (3) gives

$$\Delta Hf^{0}_{298} [\text{trans-}N_2F_2(g)] = + 19.4 \pm 1.3 \text{ kcal mole}^{-1}$$

$$\Delta Hf^{0}_{298} [\text{"active"-}N_2F_2(g)] = + 16.4 \pm 1.2 \text{ kcal mole}^{-1}$$

The "active" form is more stable thermodynamically than the trans-form of N_2F_2 by 3.0 kcal mole^{-1}. Colburn, et al. [5] reported a difference of 27 kcal mole^{-1} on the basis of measurements of the proportions of the two isomers in equilibrium mixtures at several temperatures. Their calculation was based upon the rate of change of the equilibrium constant with temperature. We have recalculated the data they reported for the equilibrium mixture at 558 °K, which they found to be about 87% "active" and 13% trans. From their average proportions we calculate for reaction (5),

$$\text{"active"-}N_2F_2 = \text{trans-}N_2F_2 \qquad (5)$$

ΔF^o_{558} = 2.1 kcal mole^{-1}. Assuming $\Delta S = 0$ and $\Delta C_p = 0$ for reaction (5) we find from their data $\Delta H^o_{298} = 2.1$ kcal mole^{-1}, in good agreement with the value we find for this reaction.

5.0 Discussion of Bond Energies in N_2F_2

Of considerable interest is the degree to which bond energies retain an additive character in different molecules.

If $2\Delta Hf^o_{298}$ (N) = 225.93 kcal mole^{-1} [8] and $2\Delta Hf^o_{298}$ (F) = 37.72 kcal mole^{-1} [9], the total binding energy of trans-N_2F_2 is 244.3 kcal mole^{-1}. This is the energy of 2 N-F bonds and one N=N bond. A value for the N=N bond in azoisopropane can be estimated from the heat of formation. From the heat of combustion of liquid azoisopropane, 1053.4 kcal mole^{-1} [10], the heat of vaporization, 8.5 kcal mole^{-1} [10], the heats of formation of $CO_2(g)$, -94.052, and of $H_2O(l)$, -68.317 kcal mole^{-1}, respectively [6], the heat of formation of azoisopropane gas is calculated to be 19.4 kcal mole^{-1}. By analogy with n-butane and isobutane, of which the latter is the more stable by 1.64 kcal mole^{-1} [11], azo-n-propane is estimated to be 3.28 kcal mole^{-1} less stable than azoisopropane and is therefore estimated to have a heat of formation of 22.7 kcal mole^{-1}. Kharasch [12] gives for the heat of combustion of liquid n-propylamine, 558.3 kcal mole^{-1} by Lemoult [13] and for the gas, 572.3 kcal mole^{-1} by Thomsen [14]. The heat of formation of the liquid is thus -31.3 kcal mole^{-1} and of the gas, -17.28 kcal mole^{-1} from these two measurements. The heat of vaporization of n-propylamine is given as 6.98 kcal mole^{-1} by Glazer and Rüland [15] and 6.879 kcal mole^{-1} by Bonnefoi [16]. If 6.9 kcal mole^{-1} is taken for the heat of vaporization of n-propylamine, Lemoult's value leads to -24.4 kcal mole^{-1} for the heat of formation of gaseous n-propylamine. The two values for the heat of formation are thus not in good agreement.

For the hypothetical reaction (6) we can calculate

$$2\ n\text{-}C_3H_7NH_2 \longrightarrow (C_3H_7N)_2 + 2H_2, \qquad (6)$$

ΔH^{o}_{298} = 57.1 kcal mole using -17.28 kcal mole for the heat of formation of n-propylamine, and 71.5 using -24.4 kcal mole^{-1}. The energy of this reaction can be taken as the sum of the bonds broken minus the energies of the bonds made.

$\Delta H = 4E(N\text{-}H) - E(N{=}N) - 2E(H\text{-}H) = 57.1$ or 71.5 kcal mole. Using E(N-H) = 93.4 kcal mole^{-1} as estimated from the heat of formation of NH_3 (-11.04 kcal mole^{-1}), and E(H-H) as 104.18 kcal mole^{-1} [6], we calculate E(N=N) as 107.9 kcal mole^{-1} or 93.8 kcal mole^{-1} using the above values for the heat of the hypothetical reaction in the same order.

Herron and Dibeler [17] in an electron impact study found the energy of dissociation of N=N in N_2F_2 to be 106 ±12 kcal mole^{-1}. This suggests the higher value of the (N=N) bond energy is the better. Using 107.9 kcal mole^{-1} for E(N=N), E(N-F) in N_2F_2 (trans) is calculated to be 68.2 kcal mole^{-1}. The lower value for E(N=N) would, of course, lead to a larger value for E(N-F).

If we assume the cis-1,2 difluorodiazine structure for the "active" N_2F_2, then two possibilities exist as extremes. Either E(N-E) is 69.7 kcal mole^{-1}, subject of course, as before, to the same possible variation as with the trans-difluorodiazine, or the N=N bond is 3 kcal mole^{-1} stronger in cis- than in trans-1,2-difluorodiazine.

On the other hand a different calculation would be required for E(N-F) if the structure is 1,1 difluorodiazine ($F_2N{=}N$).

We can consider nitrous oxide, NNO, as a related molecule containing an N=N bond in which one nitrogen is bonded only to nitrogen and the second nitrogen is bonded to a highly electronegative radical comparable to fluorine. The heat of formation, ΔHf^{o}_{298}, of N_2O is 19.49 kcal mole^{-1} [6], and of O is 59.55 kcal mole^{-1} [18]. The total binding energy of the N_2O molecule is therefore 265.99 kcal mole^{-1}, which is the sum of one N=N and one N=O bond. From ΔHf_{298} of NO, 21.60; and NO_2, 8.09 kcal mole^{-1} [6], the energies E(N=O) in these two molecules can be calculated to be 150.91 kcal mole^{-1} and 111.99 kcal mole^{-1} respectively. These energies presumably form an upper and approximate lower limit for E(NO) in N_2O, and lead to 115.07 and 153.99 kcal mole^{-1} respectively for E(N=N) in N_2O.

It will be noted that if the lower of these values for E(N=N) is taken as applying to $F_2N=N$ then E(N-F) in 1;1-difluorodiazine would be 66.1 kcal $mole^{-1}$, and that if any higher value be taken for E(N=N) then E(N-F) becomes smaller and in fact could be as low as 46.6 kcal $mole^{-1}$ if the extreme value 150.91 kcal $mole^{-1}$ be taken for E(N=N).

The suggestive point about the above discussion is that if 1,1 difluorodiazine is indeed the structure of "active"-N_2F_2, then a reason for its strikingly greater reactivity becomes plausible. The N-F bonds are the weak links in either "active"- or trans-N_2F_2 according to the above discussion, but although the heats of formation indicate that the "active"-N_2F_2 has the greater thermodynamic stability, the energy, E(N-F), in this molecule is found to be less than in trans-N_2F_2 by any of the means of calculation used. Under some assumptions suggested it would be much weaker than in NF_3. A very low N-F energy would explain the greater reactivity and also would help to explain the absence of the F_2N peak in the mass spectrometer pattern [17,19,20]. Arguments against the 1,1 difluorodiazine structures on the basis of the absence of the NF_2^+ peak and analogy to COF_2 (19) are hardly conclusive in view of the low intensity of the CF_2^+ peak from COF_2 in spite of the relatively much greater C-F bond energy, which is in the neighborhood of 116 kcal $mole^{-1}$ as compared to the NF bond here indicated.

One of the more interesting features of the current discussion of the structures of N_2F_2 isomers is that three configurations appear definitely to be possible, and bond energy arguments indicate that all should be comparably stable, but apparently only two isomers have been isolated. Thus, there is a third substance still to be found, regardless of whether the "active" isomer turns out to be cis-1,2 difluorodiazine or 1,1 difluorodiazine.

6.0 References

[1] Marantz, S., Coyle, C. F., and Armstrong, G.T., NBS Report No. 6363, April, 1959.

[2] Armstrong, G.T., Marantz, S., and Coyle, C.F., J. Am. Chem. Soc. 81, 3798 (1959).

[3] Armstrong, George T., Marantz, S. and Coyle, C. F., NBS Report No. 6584, October, 1959.

[4] Sanborn, H., J. Chem. Phys. 33, 1855 (1960).

[5] Colburn, C.C., Johnson, F.A., Kennedy, A., McCallum, K., Metzger, L.C. and Parker, C.O., J. Am. Chem. Soc. 81, 6397 (1959).

[6] Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S., and Jaffee, I., "Selected Values of Chemical Thermodynamic Properties" NBS Circular 500 (U.S. Government Printing Office, Washington 25, D. C.).

[7] Higgins, T.L., "Dissertation Abstracts," 17, 1231 (1957).

[8] Brewer, L. and Searcy, A.W., Ann. Rev. Phys. Chem. 7, 259 (1956).

[9] Stamper, J.G. and Barrow, R.F., Trans. Faraday Soc. 54, 1592-5 (1958).

[10] Coates, G.E. and Sutton, L.E., J. Chem. Soc. 1948, 1187.

[11] Rossini, F.D., Pitzer, K.S., Taylor, W.J., Ebert, J.P., Kilpatrick, J.E., Beckett, C.W., Williams, M.G., and Werner, H.G. Selected Values of Properties of Hydrocarbons, NBS Circular 461, (U.S. Government Printing Office, Washington 25, D.C., 1947).

[12] Kharasch, M.S., BS J. Research 2, 359 (1929).

[13] Lemoult, P., Ann. chim. phys. (8), 10, 395 (1907).

[14] Thomsen, J., Thermochemistry (K.A. Burke, Translator) (Longmans, Green and Co., New York, 1908).

[15] Glaser, F., and Rüland, H., Chem. Ing.-Tech. 29, 772 (1957).

[16] Bonnefoi, J., Ann chim. phys. [7] 23, 377 (1901).

[17] Herron, J.T. and Dibeler, V.H., Unpub. data, NBS, April 10, 1961.

[18] Stull, D.R. and Sinke, G.C., Thermodynamic Properties of the Elements, (American Chemical Society, Washington 6, D.C., 1956)

[19] Ettinger, R., Johnson, F.A., and Colburn, C.B., J. Chem. Phys. 34, 2187 (1961).

[20] Sanborn, R.H., J. Chem. Phys. 34, 2188 (1961).

U. S. DEPARTMENT OF COMMERCE
Luther H. Hodges, *Secretary*

NATIONAL BUREAU OF STANDARDS
A. V. Astin, *Director*

THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

WASHINGTON, D.C.

Electricity. Resistance and Reactance. Electrochemistry. Electrical Instruments. Magnetic Measurements. Dielectrics.

Metrology. Photometry and Colorimetry. Refractometry. Photographic Research. Length. Engineering Metrology. Mass and Scale. Volumetry and Densimetry.

Heat. Temperature Physics. Heat Measurements. Cryogenic Physics. Equation of State. Statistical Physics.

Radiation Physics. X-ray. Radioactivity. Radiation Theory. High Energy Radiation. Radiological Equipment. Nucleonic Instrumentation. Neutron Physics.

Analytical and Inorganic Chemistry. Pure Substances. Spectrochemistry. Solution Chemistry. Standard Reference Materials. Applied Analytical Research.

Mechanics. Sound. Pressure and Vacuum. Fluid Mechanics. Engineering Mechanics. Rheology. Combustion Controls.

Organic and Fibrous Materials. Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Plastics. Dental Research.

Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics. Electrolysis and Metal Deposition.

Mineral Products. Engineering Ceramics. Glass. Refractories. Enameled Metals. Crystal Growth. Physical Properties. Constitution and Microstructure.

Building Research. Structural Engineering. Fire Research. Mechanical Systems. Organic Building Materials. Codes and Safety Standards. Heat Transfer. Inorganic Building Materials.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics. Operations Research.

Data Processing Systems. Components and Techniques. Digital Circuitry. Digital Systems. Analog Systems. Applications Engineering.

Atomic Physics. Spectroscopy. Infrared Spectroscopy. Solid State Physics. Electron Physics. Atomic Physics.

Instrumentation. Engineering Electronics. Electron Devices. Electronic Instrumentation. Mechanical Instruments. Basic Instrumentation.

Physical Chemistry. Thermochemistry. Surface Chemistry. Organic Chemistry. Molecular Spectroscopy. Molecular Kinetics. Mass Spectrometry.

Office of Weights and Measures.

BOULDER, COLO.

Cryogenic Engineering. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Cryogenic Technical Services.

Ionosphere Research and Propagation. Low Frequency and Very Low Frequency Research. Ionosphere Research. Prediction Services. Sun-Earth Relationships. Field Engineering. Radio Warning Services.

Radio Propagation Engineering. Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation-Terrain Effects. Radio-Meteorology. Lower Atmosphere Physics.

Radio Standards. High Frequency Electrical Standards. Radio Broadcast Service. Radio and Microwave Materials. Atomic Frequency and Time Interval Standards. Electronic Calibration Center. Millimeter-Wave Research. Microwave Circuit Standards.

Radio Systems. High Frequency and Very High Frequency Research. Modulation Research. Antenna Research. Navigation Systems.

Upper Atmosphere and Space Physics. Upper Atmosphere and Plasma Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.